PATENT SPECIFICATION

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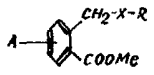
COMPLETE SPECIFICATION

A Process for the Manufacture of Aromatic Ether or Thioether Carboxylic Acids and their Salts or Esters

We, HENKEL & CIE G.M.B.H., a German Company, of 67, Henkelstrasse, Duesseldorf-Holthausen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

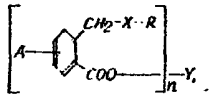
This invention relates to the production of aromatic ether or thioether carboxylic acids and their salts or esters.

According to one aspect of the invention, compounds of the general formula



are obtained. In the above formula and hereinafter, A denotes a plurality of hydrogen atoms in the aromatic ring of a corresponding number of substituents of the same or different kind, especially halogen atoms or groups containing sulphur or nitrogen by which the hydrogen atoms of the ring may be substituted, X denotes oxygen or sulphur, R denotes a substituted or unsubstituted alkyl or aryl group containing 1 to 20 carbon atoms, and Me denotes a salt-forming cation, preferably an alkali metal. In particular, residues A may be halogen atoms or nitro groups.

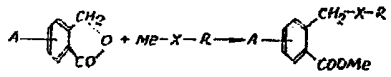
The invention further concerns the production of esters of the general formula



wherein A, X and R have their previous meanings, n is a whole number from 1—6, preferably from 1—3, and Y denotes the residue of an n-valent alcohol having 1—20 carbon atoms. R and Y can be identical.

[Price [illegible]]

In one form of the process according to the invention, a start is made from the internal ester of o-hydroxymethylbenzoic acid (phthalide) or a substituted phthalide, and this is reacted with a metal compound of an organic hydroxy- or mercapto-compound, of formula Me—X—R, preferably in the absence of water, according to the equation:



6-chlorophthalide, 4.7-dichlorophthalide or 6-nitrophthalide, for instance, may enter into consideration as the substituted phthalides.

All hydroxy or mercapto compounds, such as alcohols, phenols, and mercaptans, which form metal compounds can be converted with the acid component. Alcohols such as ethanol, butanol, n-octanol, n-dodecanol, n-hexadecanol, n-octadecanol, 2-ethylhexanol-1, 2-methylheptanol-1, 3.5.5-trimethylhexanol-1, butoxyethanol, octyloxyethanol, phenylethanol, phenoxy-ethanol, 4-chloro-phenoxy-ethanol, 2.4-dichlorophenoxy-ethanol, 4-chloro-2-cresoxy-ethanol, 2.4.5-trichlorophenoxy-ethanol, naphthyl-1-ethanol, naphthyl-1-hydroxyethanol, tetrahydrofurfurylalcohol, benzylalcohol, 1-menaphthylalcohol, chloroethanol, cyclohexanol, methylcyclohexanol, glycol, diethyleneglycol, 1.4-butanediol, 1.6-hexanediol may be mentioned by way of example.

Further, metal compounds of aromatic hydroxy-compounds such as phenol, 4-cresol, 4-chlorophenol, 2-cresol, 4-chloro-2-cresol, 2.4-dichlorophenol, 2.4.5-trichlorophenol, 3.5-xylenol, 4-isobutylphenol, 4-isooctylphenol, 4-chloro-2-benzylphenol, 2-phenylphenol, guaiacol, carvacrol, thymol, 4-phenoxyphenol, 1-naphthol, 2-naphthol, 1-chloro-2-naphthol, 4-chloro-1-naphthol, catechol, 4.4¹-dihydroxydiphenyl methane, 4.4¹-dihydroxydiphenyl-

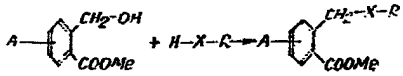
propane, 4.4¹-dihydroxydiphenylsulphone, and nitrophenols can be converted. Organic mercapto compounds which are accessible for conversion are, for example, butyl mercaptan, octyl mercaptan, benzyl mercaptan, thiophenol, 2-thionaphthol, methyl-thiouracil and mercaptobenzthiazol.

Preferably, hydroxy or mercapto compounds with 1—20 carbon atoms per molecule are treated.

By the metal compounds of organic hydroxy or mercapto compounds are meant the alcoholates, mercaptides, phenates or thiophenates of metals having a valency of 1—3, such as potassium, sodium, magnesium or aluminium, which can be obtained in the customary manner. A start is made, for example, either from the metals or their hydroxides, and in the latter case the water formed is preferably removed.

The reaction occurs when approximately equivalent quantities of the two participants in the reaction are caused to act upon each other in the presence or absence of an anhydrous solvent, preferably at an elevated temperature. The solvents employed can be inert, such as xylene, chlorobenzene or decalin. In the conversion of phenates or thiophenates, alcohols also perform useful services, i.e., higher boiling alcohols, which permit working without pressure even at higher temperatures. Finally, the hydroxy or mercapto compound to be converted can itself serve as a solvent; it is then used in excess. This process is recommended when the hydroxy or mercapto compounds are easy to distil or are otherwise easy to remove, such as, butanol and phenol.

In another form of the process according to the invention, a start is made from salts of o-hydroxymethylbenzoic acid or its substitution products, and an organic hydroxy- or mercapto-compound of formula H—X—R, and the reaction proceeds according to the equation:—



The most important reaction components are the salts of o-hydroxy-methylbenzoic acid, which can be obtained in a simple manner by dissolving the easily accessible phthalide in aqueous-alkaline-agents and, if necessary, evaporating the solution to dryness. It is also possible, however, to start from salts of ring substituted o-hydroxymethylbenzoic acids, which can be produced in a similar manner from ring substituted derivatives of phthalide, such as 6-chloro-phthalide, 4.7-dichlorophthalide or 6-nitro-phthalide. There may be considered here as salt forming bases all those, the aqueous solutions of which are capable of splitting the lactone ring of phthalide. The hydroxides of mono-, di- or tri-valent metals such as alkali, alkaline earth or earth metals are preferably used here.

The hydroxy or mercapto compounds used may be the same as those which already served as the alkoxylation components in the conversion of the phthalide or its derivatives.

The conversion is performed when approximately equivalent quantities of both participants in the reaction are caused to act upon each other in the presence or absence of a solvent at temperatures between 50 and 250° C, preferably between 100° and 200° C, care being taken to ensure that the water produced by the reaction is removed from the mixture. Inert liquids, such as toluene, xylene, chlorobenzene and decalin, which at the same time serve as entraining agents for the water to be removed, may be co-employed here as solvents. However, it is also possible to use the hydroxy or mercapto compounds which are to be converted in excess, so that they themselves act as solvents or water entraining agents. This process is to be recommended when the excess hydroxy or mercapto compound is easily removable by distillation. In carrying out the reaction, it is necessary firstly to isolate the salts of 2-hydroxymethylbenzoic acid as such. It is expedient and simplest to proceed by diluting phthalide with an equivalent amount of not over-diluted lye and then, after adding the hydroxy or mercapto compound and the dragging agent which is to be employed as well in certain cases, removing, at approximately 100° C, firstly the water introduced with the lye and then, without interruption of the reaction and at higher temperatures, the water occurring during the actual conversion. When simple phenols are used, with which no steric alterations influence the reaction, yields above 90% of the theoretical can be achieved in this way.

In individual cases, it was, surprisingly, possible to perform the conversion according to the process even in water as a solvent; thus, for example, the formation of 2-phenoxy-methyl-benzoate of sodium was achieved, even if in smaller yield, by heating a 25% aqueous solution of equivalent quantities of 2-hydroxy-methyl-benzoate of sodium and phenol for 28 hours in an autoclave at 130° C.

If it is desired to produce the esters, a start is made from the free ether- or thioether-methyl-benzoic acids, and the latter are reacted at elevated temperature with hydroxy compounds of formula Y—O—H or with corresponding poly - hydroxy compounds, under esterification conditions, in the presence or absence of known esterification catalysts. A start can, however, also be made from the salts of ether or thio-ether carboxylic acids, by causing them to act in known manner at elevated temperature and in given cases in a solvent upon the hydrogen halide esters of those hydroxy compounds, the esters of which

it is desired to produce. This way offers advantages especially when it is desired to produce esters of those hydroxy compounds which, like benzylalcohol and others, are technically obtained from the corresponding halides. The operation of saponifying the halides to the hydroxy compounds is saved in this way. Finally, it is also possible to convert the acids into halides, and to convert the halides with the hydroxy compounds in the presence of acid-binding agents.

All esterifiable aliphatic, araliphatic, aromatic or heterocyclic hydroxy compounds or mixtures thereof, which can also be polyvalent and, in given cases, substituted as desired, can be considered as alcoholic esterification components which can also be used in the form of their hydrohalic acid esters in the cases in question. They include those hydroxy compounds which are contained in the form of the residue R in the ether or thioether carboxylic acids which are to be produced in accordance with the process of the invention. In addition, they include polyvalent alcohols, such as ethylene glycol, glycerin, pentaerythritol and dipentaerythritol.

The esters which can be produced in accordance with the process of the invention are valuable plasticising, gelatinising, swelling and softness-preserving agents for the manufacture of plastic masses from vinylpolymers, polyesters and polyamides, cellulose esters and ethers, chlorinated rubber and other highly polymeric substances, and can further be employed as additions to lubricants and as fixers for scents.

EXAMPLE 1.

2-phenoxymethylbenzoic acid.

To a solution of 9.4 gm. of phenol (1/10 mole) in 100 gm. of butanol are added 2.3 gm. of metallic sodium (1/10 mole) and, after the sodium has been dissolved, 13.4 gm. of phthalide (1/10 mole). After 16 hours' boiling under a reflux condenser, the butyl alcohol is driven off, the residue is taken up in water, and the carboxylic acids formed are precipitated from the mixture as an oil by adding 50 cc. of 2 N. hydrochloric acid. After heating for a short time, the mixture is cooled and the oil, which solidifies to a crystalline mass in the cold, is isolated. The oil is treated in a mortar with cold 5% soda solution, in which any phthalide which may still be present (in the conversion of higher phenol-homologues, these as well) is to a great extent insoluble. Separation is performed by filtration, preferably with the addition before filtering of decolourising carbon. The raw 2-phenoxymethylbenzoic acid, which is precipitated from the soda solution in the cold by dropping in dilute hydrochloric acid, is filtered, and, after drying, freed by a treatment with ether from small quantities of accompanying high-melting acid substances which are soluble in ether. By expelling the ether, 9—10 gm. of pure 2-phenoxymethylbenzoic acid are obtained. The acid melts in conformity with the data of Oppé (Berichte der deutschen chemischen Gesellschaft, Vol. 46, page 1096) at melting point = 126.5°C (after crystallising from benzene).

If, instead of butanol, the same quantity of cyclohexanol is used as a solvent and condensing is effected by heating to 200°C for 6 hours, 11—12 gm. of pure 2-phenoxymethylbenzoic acid are obtained, subsequent processing details being otherwise similar.

EXAMPLE 2.

2-(2¹-methyl-phenoxymethyl)-benzoic acid.

If the process of Example 1 is varied by causing 10.8 gm. of o-cresol (1/10 mole) to react instead of 9.4 gm. of phenol, but using similar subsequent processing pure 2-(2¹-methyl-phenoxymethyl)-benzoic acid of melting point 152°C (crystallised from benzene or xylene) is obtained in slightly smaller yield.

EXAMPLE 3.

2-phenylthiomethyl-benzoic acid.

To a solution of 11.0 gm. of thiophenol (1/10 mole) in 100 cc. of butanol are added 2.3 gm. of sodium (1/10 mole) and, after the sodium has dissolved, 13.4 gm. of phthalide. After 8 hours' stirring at 100°C, the butyl alcohol is distilled off, the crystalline residue is taken up in water, animal charcoal is added, and filtering is performed. The 2-phenyl-thiomethyl-benzoic acid precipitated by adding 50 cc. of 2 N. hydrochloric acid is recrystallised from benzene or dilute alcohol. 21.8 gm. of the acid with a melting point of 112°C are obtained (crystallising from benzene).

EXAMPLE 4.

2-butoxymethyl-benzoic acid.

13.4 gm. of phthalide are added to a solution of 2.3 gm. of sodium (1/10 mole) in 100 cc. of butanol; heating is effected for 16 hours under a reflux condenser. The residue, freed of butanol, is dissolved in 100 cc. of water, charcoal is added the solution is filtered and 50 cc. of hydrochloric acid are added to the filtrate. The oil accruing here, which solidifies to a crystalline mass in the cold, is treated as described in Example 1 with a 5% soda solution, and the raw 2-butoxymethyl-benzoic acid is precipitated in the cold from the solution so obtained by the addition of acid, where necessary after the portions which have remained insoluble have been separated off. Small quantities (approximately 0.5 gm.) of high melting portions, which are contained in the raw acid, are removed by redissolving in ether, in which said portions are insoluble. The 2-butoxymethyl-benzoic acid remaining after the ether has been expelled is subsequently obtained in a pure state as regards analysis and melting point, the later being 63—64°C, after recrystallisation from 20% acetic acid.

EXAMPLE 5.

2-(n-octyloxymethyl)-benzoic acid.

Using the same general procedure as in the above Example and using 100 gm. of n-octanol instead of butanol, 2-(n-octyloxymethyl)-benzoic acid is obtained and is subsequently obtained analytically pure by recrystallisation from 60% acetic acid. Melting point=66—67°C.

EXAMPLE 6.

2-phenoxymethyl-benzoic acid.

A mixture of 17.4 gm. of 2-oxymethyl-benzoate of sodium (1/10 mole), 9.4 gm. of phenol (1/10 mole) and 50 cc. of xylene is heated to boiling in an esterification appliance, with stirring, until the quantity of water collecting in the separator no longer increases, for which some 6—8 hours are necessary. The xylene and minute portions of unconverted phenol are removed by steam distillation, and the aqueous solution remaining is mixed with 50 cc. of 2 N. hydrochloric acid, if necessary after decolourising with charcoal.

In order to free the crystalline mass accruing here from residues of unchanged 2-hydroxy-methylbenzoic acid, the acid solution is heated for a short time before filtration, whereby the 2-hydroxymethylbenzoic acid changes into phthalide, which is insoluble in soda, and as such can be separated off by subsequent treatment with 50 cc. of 2 N soda solution. The acid which separates out in a crystalline form when the soda solution is acidified still contains small quantities of a high melting accompanying substance, which can be liberated by treatment with ether, in which it is insoluble. From the ether solution, 11.5 gm. of 2-phenoxymethyl-benzoic acid are obtained, and can be subsequently purified by recrystallisation from benzene, chloroform or dilute alcohol. The acid melts at 126.5°C. in conformity with data in literature.

EXAMPLE 7.

2-(2¹-methyl-phenoxymethyl)-benzoic acid.

Using the same general procedure as in Example 6 and using 10.8 gm. of o-cresol (1/10 mole) instead of phenol, 14.5 gm. of 2-(2¹-methylphenoxymethyl)-benzoic acid are obtained. Recrystallised from chloroform or benzene, the acid, which occurs in the form of colourless needles, melts at 153°C.

EXAMPLE 8.

2-(4¹-methyl-phenoxymethyl)-benzoic acid.

When recrystallised from dilute alcohol, the 2-(4¹-methyl-phenoxymethyl)-benzoic acid obtained in the form of white needles when p-cresol is used in place of o-cresol in Example 7 has a melting point of 124°C.

EXAMPLE 9.

2-(2¹-methyl-4¹-chloro-phenoxymethyl)-benzoic acid.

If 17.4 gm. of 2-hydroxymethylbenzoate of sodium (1/10 mole) and 14.2 gm. of 4-chloro-2-cresol (1/10 mole) are heated to boiling in 100 cc. of xylene for 20 hours, with stirring, in the manner described above, until 1.5 cc. of water have been split off, and the components which are soluble in water are then withdrawn from the mixture by extraction with water, there are then obtained, on acidifying the aqueous extract, 19 gm. of raw 2-(2¹-methyl - 4¹ - chloro-phenoxymethyl)-benzoic acid, which is freed of phthalide or ether-insoluble impurities in the manner described in Example 1 by a treatment with soda solution and then with ether.

EXAMPLE 10.

2-(2¹,4¹-dichloro-phenoxymethyl)-benzoic acid.

In the above Example, if the 4-chloro-2-cresol employed is replaced by 16.3 gm. of 2.4-dichlorophenol (1/10 mole), there is obtained in the same yield, with similar subsequent processing, 2-(2¹,4¹-dichloro-phenoxymethyl)-benzoic acid, which can be purified by recrystallising from a mixture of equal parts of benzine and benzene and which melts pure at 167°C.

EXAMPLE 11.

2-(naphthyl-1¹-oxymethyl)-benzoic acid.

If equimolar quantities of 1-naphthol and 2-hydroxymethylbenzoate of sodium are heated as in the foregoing Examples in the presence of xylene as the diluting and dragging agent until the splitting off of water has terminated, then, with the usual subsequent processing, 2-(naphthyl-1-oxymethyl)-benzoic acid, of melting point 156—157°C, and which can be recrystallised from benzene is obtained.

EXAMPLE 12.

2-(2¹-mercaptobenzthiazol-S-methyl)-benzoic acid.

16.7 gm. of 2-mercaptobenzthiazol (1/10 mole) and 17.4 gm. of 2-hydroxymethylbenzoate of sodium are heated for 8 hours in 50 cc. of xylene until the splitting off of water has terminated. After cooling, the 2-(2¹-mercaptobenzthiazol-S-methyl)-benzoate of sodium formed is extracted from the mixture by shaking with water, and the acid accruing on acidifying is purified, as in the foregoing Examples, by treatment with a 10% soda solution. 22 gm. of the acid are obtained and in certain cases recrystallised from benzene (melting point=168—169°C).

EXAMPLE 13.

2-(4¹-i-heptyl-phenoxymethyl)-benzoic acid.

Starting from 4-i-heptylphenol (of melting point=38°C) and an equivalent quantity of 2-hydroxymethylbenzoate of sodium, 2-(4¹-i-heptyl-phenoxymethyl)-benzoic acid was produced similarly to the foregoing Examples, which acid, recrystallised from 70% acetic acid, possesses a melting point of 104—105°C.

EXAMPLE 14.

S-2-carboxybenzyl-thio-glycolic acid.

17.4 gm. of 2-hydroxymethylbenzoate of sodium (1/10 mole), 9.6 gm. of a 95% thioglycolic acid (1/10 mole), 50 cc. of 2 N. caustic soda solution, and 100 cc. of xylene

are heated on an oil bath to 160—170°C, with efficient stirring, until all water is azeotropically removed and the salts suspended in the xylene have solidified to a hard mass, which is the case after 2—3 hours. These salts, after the removal of the xylene, are dissolved in approximately 150 cc. of water, hydrochloric acid is added, and the crystalline precipitate produced is brought into solution by boiling for a short time. The raw acid crystallising out on cooling is freed from small phthalide portions still contained in it by dissolving in dilute soda solution and filtration in the manner previously described. When the soda solution is acidified, 9.4 gm. of S-2-carboxy-benzyl-thioglycolic acid are obtained. After recrystallising the acid again from water, acetic acid, and butyl acetate, the pure acid obtained melts at 146°C.

EXAMPLE 15.

2-(4¹-tertiary-butylphenoxymethyl)-benzoic acid.

A mixture of 19 gm. of 2-hydroxymethyl-benzoate of potassium (1/10 mole) 15 gm. (1/10 mole) of 4-tertiarybutylphenol of melting point 94°C and 100 cc. of xylene are heated to boiling under reflux and separation of water until the quantity of water split off no longer increases (approximately 20 hours). The 2-(4¹-tertiary-butylphenoxymethyl)-benzoic acid which is isolated from the reaction mixture in a quantity of 16.5 gm. in the manner described in Examples 4 and 1 can be recrystallised from benzine (boiling point 100—140°C) and 70% acetic acid and melts pure at 140°C.

EXAMPLE 16.

2¹,2¹¹-bis-2-phenoxymethyl-benzoic acid.

18.6 gm. of 2.2¹-diphenol (1/10 mole) and 38 gm. of 2-hydroxymethylbenzoate of potassium (2/10 mole) are converted in the presence of 100 cc. of xylene as a dragging or diluting agent by heating for 20 hours, and, after cooling, the mass is mixed with 100 cc. of water. After the xylene layer has been separated off, the acid portions, which separate here in an oily form, are precipitated from the aqueous solution by adding hydrochloric acid. They are then dissolved in dilute soda solution, and the portions of unconverted 2.2¹-diphenol (approx. 15.5 gm.) contained therein are removed by an exhaustive extraction with ether. After the ether residues have been expelled, there is obtained from the soda solution, by acidifying, a colourless crystalline deposit, which is isolated (26.0 gm.). The acid, which is purified by repeated recrystallisation from a very large amount of glacial acetic acid and 70% dimethylformamide, melts at 250°C and corresponds analytically to the composition $C_{28}H_{22}O_6$, so that it is to be regarded as 2¹,2¹¹-bis-2-phenoxymethyl benzoic acid.

EXAMPLE 17.

134 gm. of phthalide (1 mole) are dissolved, with heating, in 100 gm. of 40% caustic soda solution in an esterification appliance. To this solution are added 183 gm. (1.5 mole) of a technical xylenol mixture having the hydroxyl number 461, and 40 cc. of xylene, the latter as a dragging agent to facilitate the removal of water. The clear mixture is first heated, with constant stirring, at temperatures around 100° to 120° C until the water introduced with the caustic soda is removed, and the temperature is then raised to 180—190° C. After the reaction has lasted four hours at this temperature, the conversion is complete and the theoretical quantity of water (18 cc.) has been split off.

After cooling the mixture to 70° C, 500 cc. of 2N hydrochloric acid are added thereto with thorough intermixing, and the aqueous solution of sodium chloride is separated off. The oil remaining is freed from the xylene and the xylenol, which is used in excess, by distillation under reduced pressure. The remaining isomeric mixture of the raw 2-xylenoxymethyl-benzoic acids (242 gm.) can be purified by distillation under fairly high vacuum. 215 gm. of a light yellow oil which is viscous in the cold and which solidifies to a crystalline mass on standing for a lengthy period are then obtained. B.p = 233—247° C at 3 mm. Hg.

EXAMPLE 18.

2-(2¹-cresoxymethyl)-benzoic acid-(2-ethylhexyl)-ester.

A mixture of 242 gm. of 2-(2¹-cresoxymethyl)-benzoic acid (1 mole), 195 gm. of 2-ethylhexanol (1.5 mole) and 40 gm. of xylene is heated in an esterification appliance to 180°—195° C until the splitting off of water is terminated and the acid number of the mixture is below 3. The esterification product obtained is freed of the residues of unchanged acid by treatment with 2% caustic soda solution, and purified by distillation. 317 gm. of pure 2-(2¹-cresoxymethyl)-benzoic acid-(2-ethylhexyl)-ester are obtained. The ester is a pale yellow liquid of boiling point = 221—224° C at 1 mm. Hg. and saponification number 160 (saponification number calculated = 158).

EXAMPLE 19.

2-xylenoxymethyl-benzoic acid-n-octylester.

256 gm. of 2-xylenoxymethyl-benzoic acid (1 mole), produced from a technical xylenol mixture and phthalide, in the manner described in Example 17, are esterified with 195 gm. of n-octanol (1.5 mole) as in the above Example. 334 gm. of pure xylenoxymethyl-benzoic acid-n-octylester are obtained as a yellowish liquid of B.p. = 223—248° C at 1 mm. Hg., and of having a saponification number 154 (saponification number calculated: 152).

EXAMPLE 20.

2-xylenoxymethyl-benzoic acid-butoxy-ethylester.

To a solution, produced by warming, of 134 gm. of phthalide (1 mole) in 100 gm. of 40% caustic soda solution are added 183 gm. of a technical xylenol mixture having a hydroxyl number 461 (1.5 mole) and 40 cc. of xylene, which is intended to serve in the subsequent conversion as a dragging agent for the water to be removed. After an esterification attachment has been put on, the mixture is first heated, with continued stirring, to temperatures of 100°—120° C in order to remove azeotropically the water introduced with the caustic soda solution, and the temperature is then raised to 180—210° C. After 4 hours' heating, a quantity of water of reaction (18 gm.) corresponding to the theoretical has been split off and conversion is terminated. After cooling to 70° C, 500 cc. of 2N hydrochloric acid are added, and after thorough mixing, the aqueous solution of sodium chloride is separated off.

Butoxy-ethanol (2 moles) is now added to the reaction material and esterification is carried out, with stirring, at 180° C until no more water collects in the separator and the acid number of the reaction mixture has dropped below 4. The xylene and the xylenol, which is used in excess, and the butoxy-ethanol, together with a minor quantity of phthalide, are removed by fractional distillation under reduced pressure, and the 2-xylenoxymethyl-benzoic-acid-butoxyethyl ester (B.p. = 224—244° C at 1 mm. Hg.) formed is then distilled under fairly high vacuum. Small residues of acid components are removed by refining with dilute caustic sola solution. 292 gm. of pure ester of saponification number 161 (saponification number calculated: 157) are obtained.

EXAMPLE 21.

2-(4¹-cresoxymethyl)-benzoic acid benzylester.

Corresponding to the procedure of the foregoing Example, 134 gm. of phthalide (1 mole), dissolved in 100 gm. of 40% caustic soda solution, are converted with 108 gm. of p-cresol (1 mole) in the presence of 50 cc. of xylene, the final temperature being 210° C, until the water introduced and the water formed during the reaction have been entirely removed. 140.5 gm. of benzylchloride (1 mole) are added to the mixture at 180° C, and heating is continued for four hours to 210° C. The mass thickens owing to the sodium chloride which separates out and which, after termination of conversion, is removed together with small quantities of unconverted phthalide and p-cresol by thorough washing with dilute caustic soda solution and water. The 2-(4¹-cresoxymethyl)-benzoic acid-benzyl ester formed can be isolated and purified by distillation under reduced pressure and is a pale yellow coloured liquid of B.p. = 248—253° C at 1 mm. Hg. and saponification number 170 (saponification number calculated: 168) which solidifies to a crystalline mass in the cold. 250 gm. are obtained, melting point (from alcohol) = 42° C.

EXAMPLE 22.

2-phenylthiomethyl-benzoic acid-octylester.

244 gm. of 2-phenylthiomethyl-benzoic acid of melting point 112° C (1 mole) are esterified at 180° C. in known manner with 390 gm. of n-octanol in the presence of a little xylene. After removal of the excess alcohol and unchanged acid, the 2-phenyl-thiomethyl-benzoic acid-n-octylester formed is obtained as a yellowish liquid of saponification number 160 (saponification number calculated: 157) which can no longer be distilled and which does not solidify in the cold.

EXAMPLE 23.

2-phenoxymethyl-benzoic acid-phenylester.

To 24.6 gm. of 2-phenoxymethyl-benzoic acid chloride (1/10 mole), which was obtained by the action of phosphorous pentachloride upon the free acid, is added a mixture of 9.4 gm. of phenol (1/10 mole) 50 gm. of acetone, and 10 gm. of 40% caustic soda solution, and heating to boiling is effected for several hours. The 2-phenoxymethyl-benzoic acid-phenylester formed proves to be difficultly saponifiable and melts at 69° C after recrystallisation from a little petroleum ether.

What we claim is:—

1. In the manufacture of aromatic ether or thioether carboxylic acids and of their salts and esters, the process comprising reacting the internal ester of a substituted or unsubstituted *o*-hydroxymethyl-benzoic acid with a metal compound of an organic hydroxy- or mercapto-compound, of general formula Me—X—R, in which formula the symbols Me, X and R have the significance hereinbefore set forth, and thus obtaining a salt of an aromatic ether or thioether carboxylic acid.

2. A process as claimed in claim 1, in which the internal ester is phthalide.

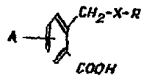
3. A process as claimed in either of claims 1 and 2, in which said metal compound of an organic hydroxy- or mercapto-compound is prepared *in situ* by employing a mixture of an organic hydroxy- or mercapto-compound of general formula H—X—R, in which formula the symbols X and R have the significance hereinbefore set forth, with an alkali metal hydroxide or with an alkali metal.

4. In the manufacture of aromatic ether or thioether carboxylic acids and of their salts and esters, the process comprising reacting a salt of a substituted or unsubstituted *o*-hydroxymethyl-benzoic acid with an organic

hydroxy- or mercapto-compound of general formula H—X—R, in which formula the symbols X and R have the significance hereinbefore set forth, and thus obtaining a salt of an aromatic ether or thioether carboxylic acid.

5. A process as claimed in any of claims 1 to 4, in which said salt of an aromatic ether or thioether carboxylic acid is subsequently converted into the free acid.

6. A process for the production of esters of aromatic ether or thioether carboxylic acids, comprising reacting an acid of formula:



in which formula the symbols X, R and A have the significance hereinbefore set forth, at elevated temperature and under esterification conditions with an organic hydroxy-compound of formula Y—O—H, in which formula the symbol Y has the significance hereinbefore set forth, or a corresponding poly-hydroxy compound.

7. A process as claimed in claim 6, in which the acid is in the form of a salt thereof and instead of the organic hydroxy-compound, an ester thereof with a hydrogen halide is employed.

8. A process as claimed in claim 6, in which the acid is in the form of a corresponding halide and the reaction takes place in the presence of an acid-binding agent.

9. Processes for the manufacture of aromatic ether or thioether carboxylic acids or of their salts or esters, substantially as hereinbefore described with reference to the Examples.

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